ENDOSULFAN AND CHLORTHAL-DIMETHYL RESIDUES IN SOIL AND SEDIMENT OF MONTEREY COUNTY

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ENVIRONMENTAL HAZARDS ASSESSMENT PROGRAM

STATE OF CALIFORNIA
Department of Food and Agriculture
Division of Pest Management, Environmental Protection and Worker Safety
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ENDOSULFAN AND CHLORTHAL-DIMETHYL RESIDUES IN SOIL AND SEDIMENT OF MONTEREY COUNTY

BY

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ABSTRACT

The California State Mussel Watch Program (SMW) has detected residues of endosulfan (Thiodan®) in Elkhorn Slough of Monterey County every year since 1979, and chlorthal-dimethyl (Dacthal®) every year since 1980. Elkhorn Slough contains a state ecological reserve and wildlife sanctuary which receives freshwater from agricultural runoff in the Moss Landing drainage area as well as saltwater from Monterey Bay. The offsite movement of chlorthal-dimethyl and endosulfan in particular (due to its extreme toxicity to fish and aquatic organisms), is of environmental concern because of potential impacts on the ecological reserve. In response, the Environmental Hazards Assessment Program of the California Department of Food and Agriculture conducted this study to identify agricultural drains in the Moss Landing drainage area that are potential sources of endosulfan and chlorthal-dimethyl contamination occurring in Elkhorn Slough.

Soil and sediment samples were collected in 1986 from the Moss Landing drainage area and analyzed for endosulfan and chlorthal-dimethyl. The formulated product of endosulfan contains two stereoisomers, endosulfan I and endosulfan II. In addition, the principal breakdown product of environmental concern is endosulfan sulfate. The samples were analyzed for all three of these forms of endosulfan. Analysis of these samples documented that 58% of the soil samples and 52% of the sediment samples contained some form of endosulfan. Peak concentrations of endosulfan I were 310 ug/kg in soil and 52 ug/kg in sediment (all concentrations are reported on a dry weight basis). Peak concentrations of endosulfan II were 960 ug/kg in soil and 160 ug/kg in sediment and for endosulfan sulfate they were 1300 ug/kg in soil and 160 ug/kg in sediment. The Old Salinas River and Moro Cojo, Reclamation and Tembladero Sloughs were identified as probable sources of endosulfan contamination from an examination of endosulfan use and the distribution of contaminated soil and sediment samples. Water from the three sloughs drains into the Old Salinas River which then empties into the lower portion of Elkhorn Slough.

Chlorthal-dimethyl was detected in 39% of the soil samples and 12% of the sediment samples taken from the Moss Landing drainage area. Peak concentrations were 690 ug/kg in soil and 25 ug/kg in sediment. Chlorthal-dimethyl residues were predominantly found in samples from Blanco Drain and agricultural areas adjacent to Elkhorn Slough.

In addition to sampling soil and sediment in the Moss Landing drainage area, soil samples were collected in agricultural areas of the Salinas and Carmel River Valleys of Monterey County to examine pesticide distributions. Endosulfan I was detected in 8% of these soil samples while endosulfan II and sulfate were detected in 9 and 27% of the soil samples, respectively. Forty-seven percent of the soil samples contained residues of chlorthal-dimethyl. Chlorthal-dimethyl residues were more evenly distributed throughout the agricultural areas of Monterey County. The large number of soil samples found positive for chlorthal-dimethyl residues is cause for concern considering soil samples were collected at random and sample collection was not correlated with season of highest use. In order to explain these results, additional studies on the half-life of chlorthal-dimethyl in California soil and its mechanisms of off-target movement are the subjects of a current investigation.

ACKNOWLEDGEMENTS

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DISCLAIMER

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

INTRODUCTION

The California State Mussel Watch Program (SMW) has monitored the environmental quality of Monterey Bay and adjacent drainage since 1977, using bi-valve mollusks as bio-indicators of specific pollutants. Endosulfan I[1] was first detected at 24 ug/kg (dry weight) in transplanted bay mussels (Mytilus californianus) collected from Elkhorn Slough in 1979 (Stephenson et al., 1980). Monitoring in 1980-81 indicated a possible increase in endosulfan I residues with concentrations reported at 140 ug/kg (dry wt.) (State Water Resources Control Board, 1982). In 1982-83, a site specific survey was established to investigate this as well as possible increases in other pesticide concentrations. This survey, which was expanded in the 1983-84 program, detected the highest residues of total endosulfan (endosulfan I + endosulfan II + endosulfan sulfate) and chlorthal-dimethyl in the history of the Mussel Watch Program; 24,500 and 8600 ug/kg (dry weight), respectively, in transplanted fresh water clams (Corbicula fluminea) collected from Reclamation Slough (Hayes and Phillips, 1984).

Endosulfan and chlorthal-dimethyl (1,4,5,6,7,7,-hexachloro-8,9,10-trinorborn-5-en-2,3-ylenedimethyl sulphite and dimethyl tetrachloroterephthalate, respectively) are pesticides used in the Moss Landing drainage area of Monterey County. This area is a highly productive agricultural region with an extensive network of drains and sloughs. The use of endosulfan and chlorthal-dimethyl combined with the flow of these water systems to Elkhorn Slough and Monterey Bay contribute to contamination of the areas's marine and freshwater ecology.

Action and tolerance levels have not been established by the U.S. Food and Drug Administration for endosulfan and chlorthal-dimethyl in fish and shellfish. Consumption guidelines, set by the Department of Health Services, are also non-existent for edible portions of these organisms (personal communication, Anna Fan, Department of Health Services).

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1. The formulated product of endosulfan consists of two stereoisomers, endosulfan I and II. The degradation product of primary concern is endosulfan sulfate (Ali, et al., 1984).

Endosulfan and chlorthal-dimethyl are presently in the process of registration re-evaluation by both the EPA and CDFA. The concern of endosulfan's extreme toxicity to fish and related fishkills, reported by the Department of Fish and Game (DFG), first initiated its re-evaluation. A rat teratology study, received by CDFA Pesticide Registration Branch, shows endosulfan as a possible weak teratogen. Concerns also exist regarding rat oncogenicity. The detection of chlorthal-dimethyl on crops where its use is not registered for, as well as over tolerance on crops where its use is registered, concerned CDFA Pesticide Use Enforcement and initiated the re-evaluation process (personal communication, Ann Prichard, Pesticide Registration Branch).

In response to environmental concerns, the Environmental Hazards Assessment Program of CDFA conducted a soil/sediment survey to identify agricultural drains in the Moss Landing drainage area that are likely sources of contamination occurring in Elkhorn Slough. In addition a soil survey was conducted to determine the general distribution of endosulfan and chlorthal-dimethyl in soils from agricultural areas of Monterey County.

MATERIALS AND METHODS

Study Area and Design

Soil/Sediment Survey - Moss Landing Drainage Area

Twenty sites were located in the Moss Landing drainage area for the collection of soil and companion sediment samples. This area includes Blanco Drain, Salinas and Old Salinas Rivers, Elkhorn, Moro Cojo, Reclamation, Alisal and Tembladero Sloughs (Fig. 1). Soil samples were taken in agricultural fields and sediment samples were collected in adjacent drains that had year round flow and lacked tidal influence.

Soil Survey - Salinas and Carmel River Valleys

Seventy-three of the 749 township/range-sections (sections) in the Salinas River Valley were selected as soil survey sites using a random number table. Within each section, an agricultural field was chosen at random upon arrival. If locating or gaining access to a field was impossible, the nearest suitable

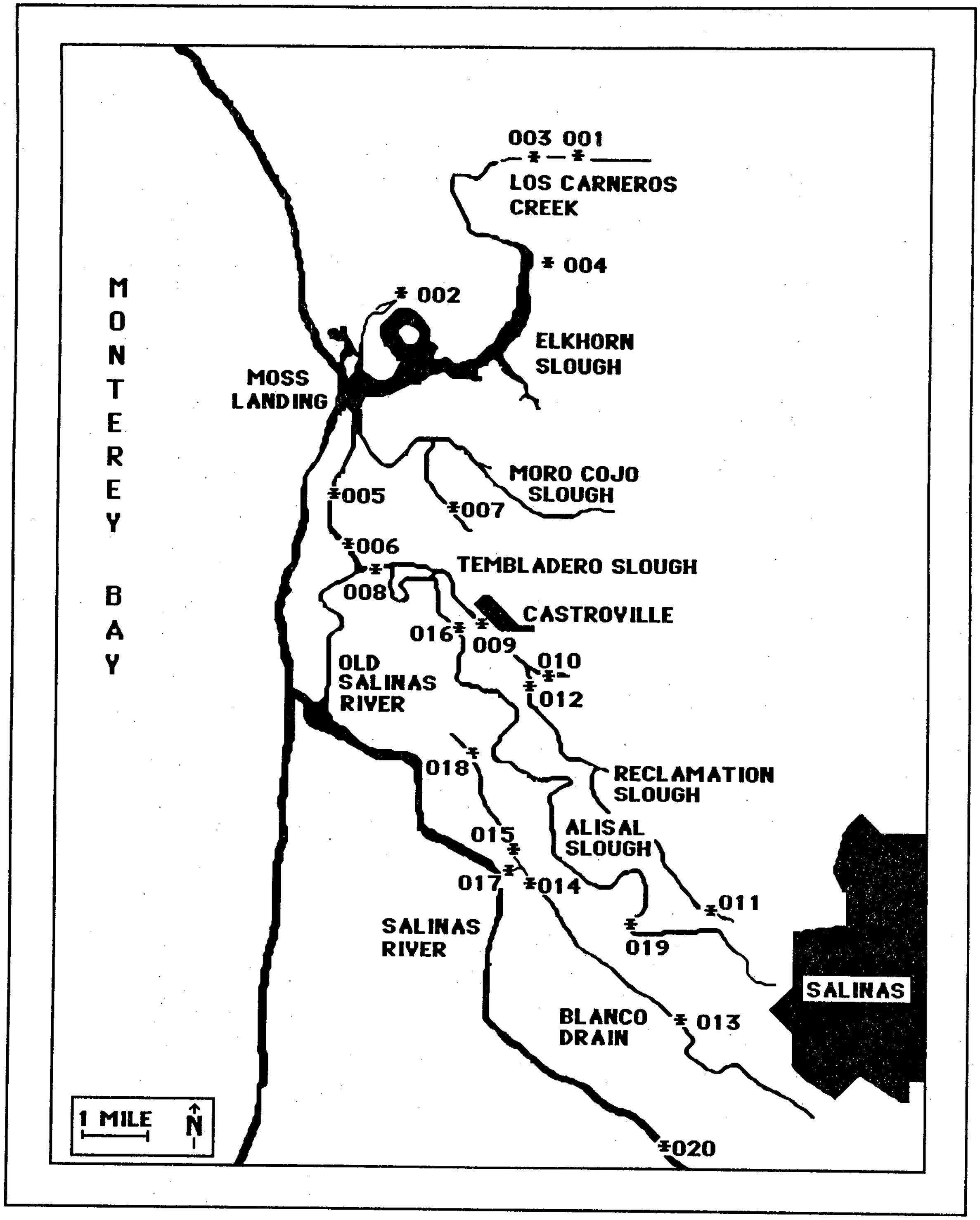

FIG. 1. SOIL/SEDIMENT MONITORING SITES IN THE MOSS LANDING DRAINAGE AREA OF MONTEREY COUNTY, CALIFORNIA, 1986

section was selected. Two additional sites were selected and sampled in the Carmel River Valley, bringing the total number of soil survey sites to 75 (Fig. 2).

Sample Collection

Soil

Soil samples, each consisting of five subsamples, were collected from agricultural fields within an area measuring 10 x 20 meters. A five meter buffer zone was allowed at field borders to avoid edge effects. Samples were collected in glass jars using a stainless steel tube with a length and inner diameter of 15.2 and 5.9 cm, respectively. Soil cores were collected at 5-cm depths and taken from seed beds whenever possible. Sample jars were placed on dry ice. Two replicates and single samples were collected for soil/sediment and soil surveys, respectively.

Sediment

Sediment samples were collected using a Wildco Instrument Model 2321-A10 sediment sampler. Each sample consisted of five subsamples randomly collected along a twenty meter transect parallel to the bank of the watercourse. Inversion of the sampler barrel allowed the sediment core to slide out onto an aluminum covered cutting board. The top 5 cm were cut and removed with a stainless steel spatula, put in a glass jar and placed on wet ice. Replicates were collected at each site.

Chemical Analysis

The California Department of Food and Agriculture, Laboratory Services Branch in Sacramento, was originally selected as the primary laboratory responsible for both soil and sediment analyses. Due to an emergency, CDFA could only complete sediment analyses. Soil samples were analyzed by the Agriculture and Priority Pollutants Laboratory (APPL) in Fresno. Sediment concentrations were reported in ug/kg, dry weight with a minimum detection limit of 8.8 ug/kg. Soil concentrations were reported in ug/kg, dry weight with minimum detection limits of 4.4 ug/kg for endosulfan I, II and chlorthal-dimethyl and 8.8 ug/kg for endosulfan sulfate. For analytical details, see Appendices I and II.

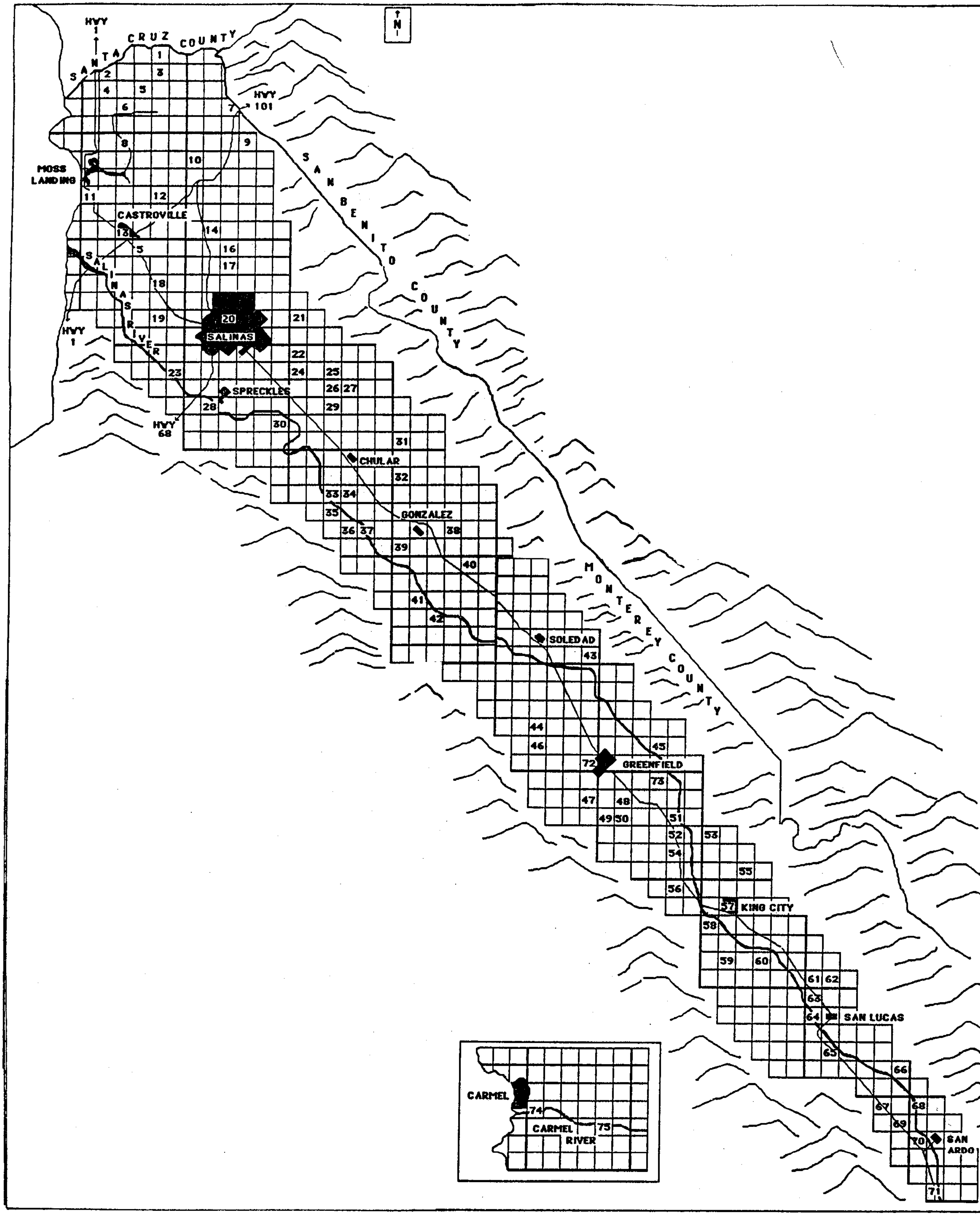

FIG. 2. SOIL SURVEY MONITORING SITES IN THE SALINAS AND CARMEL RIVER VALLEYS OF MONTEREY COUNTY, CALIFORNIA, 1986.

Quality Control

Quality control samples were analyzed for method validation and ongoing quality assurance. A complete description of the Quality Control Program is entered in Appendix III.

Data Analysis

Information concerning surface water flow, land drainage patterns and hydrologic boundaries for waterways in the Moss Landing drainage area was obtained from the Monterey County Flood Control Office. Hydrologic areas were then identified, mapped and overlaid with the area's sections. Endosulfan use in each hydrologic area was totaled using information in the Pesticide Use Report (PUR) database (CDFA, 1985 and 1986) to determine the hydrologic area contributing the largest amount of endosulfan to waters in this region. Pesticide use calculations could not be made for chlorthal-dimethyl since its use is unrestricted in California, therefore PUR information is unavailable. (The use of restricted materials in California usually requires that a permit be obtained from the county agricultural commissioner and the application reported to CDFA. From these use reports, CDFA summarizes application location, acreage involved and pounds of pesticide applied, among other details, in the PUR database.)

RESULTS AND DISCUSSION

Moss Landing Drainage Area

Pesticide and Land Use

Endosulfan use was highest in sections along the Old Salinas River and Moro Cojo, Tembladero, Reclamation and Alisal Sloughs (Tables 1 and 2). Hydrologic areas of highest endosulfan use were Reclamation Slough followed by Old Salinas River, Tembladero Slough and Moro Cojo with 4927, 3422, 1784 and 1510 kg active ingredient applied in each area, respectively (Table 2). Pesticide applications reported in Monterey County were confounded by the fact that section boundaries are not clearly mapped in this area leading to inconsistencies in use reporting. For example, according to our map, which had section boundaries estimated by personnel from the Monterey County Agricultural Commissioner's Office, site five occurred in section 13S01E-25, which was located in the midst of artichoke fields. However, neither endosulfan use nor artichokes were reported for this section in the PUR database (CDFA 1985 and 1986). Therefore, information in the PUR database from this area must be viewed qualitatively.

Predominant crops in this area (based on estimated crop acreage from land use maps) were artichokes, cole crops (e.g. cauliflower and broccoli), strawberries and lettuce (Figure 3). Endosulfan is registered for use on all five crops whereas chlorthal-dimethyl is registered only on cauliflower, broccoli and strawberries. A major use of endosulfan is for the control of plume moth on artichokes, for which repeated applications occur about once every 3 weeks. Use of endosulfan on strawberries is rare, since applications are restricted to once every 35 days during the long fruiting season. The major use of chlorthal-dimethyl is for weed control in cauliflower and broccoli fields (personal communication, Joel Trumbo, Monterey County Agricultural Commissioner's Office).

Drainage Patterns

Elkhorn Slough, which contains a state ecological reserve and wildlife sanctuary, is an estuary continually flushed by tidal action. Fresh water input comes from Carneros and Watsonville Creeks (ABA Consultants, 1987).

Table 1. Site locations, endosulfan use , crop reported in the pesticide use report and crop present at time of sampling in the Moss Landing Drainage area.

			1985		1986		
Site	T/R-S[a]	Location	Use[b]	PUR[c] Crop	Use[b]	PUR[c] Crop	Site[d] Crop
1	12S02E-27	Elkhorn Slough	0		0		ST,CO
2	13S02E-07	Elkhorn Slough	0		0		CA
3	12S02E-28	Elkhorn Slough	0		0		TO
4	13S02E-04	Elkhorn Slough	0		0		ST
5	13S01E-25	Old Salinas Riv.	0		0		A
6	13S02E-30	Old Salinas Riv.	974	A,L,S	794	A	A
7	13S02E-29	Moro Cojo	141	A	366	A	A
8	13S02E-31	Tembladero Sl.	357	A	992	A	A
9	13S02E-32	Reclamation Sl.	753	A	342	A	
10	14S02E-04	Reclamation Sl.	85	A	89	A	A
11	14S02E-24	Reclamation Sl.	57	L	16	B	A
12	14S02E-04	Reclamation Sl.	85	A	89	A	A
13	14S02E-36	Blanco Drain	60	L	43	C,L,B	C
14	14S02E-21	Blanco Drain	0		0		CE
15	14S02E-21	Blanco Drain	0		0		
16	13S02E-32	Alisal Slough	753	A	342	A	A
17	14S02E-21	Blanco Drain	0		0		CE
18	14S02E-08	Blanco Drain	98	A	88	A	
19	14S02E-26	Alisal Slough	9	C,CE	0		
20	15S02E-12	Salinas River	0		0		

a. Township/Range-Section (section).
b. Endosulfan use is in kg active ingredient per section.
c. Crops reported in these columns were from the Pesticide Use Data base (CDFA, 1985 & 1986). Abbreviations are A = artichokes, B = broccoli, C = cauliflower, CA = cabbage, CE = celery, CO = corn, L = lettuce S = squash, ST = strawberries and TO = tomatoes. Blanks indicate crops were not listed in the Pesticide Use Report.
d. Crops reported in these columns (see letter designations above) were present at sampling sites.

Table 2. Endosulfan use summarized by hydrologic area.

Hydrologic Area	T/R-S Composition[a]	1985[b]	1986[b]
Elkhorn Slough	12S/02E-20,21,22,23,24,25,26, 27,28,29,32,33,34,35,36. 13S/02E-1,2,3,4,5,6,7,8,9,10, 11,12,15,16,17,18.	946	545
Moro Cojo	13S/02E-13,14,19,20,21,22,23, 24,25,26,27,28,29.	1990	1510
Reclamation Slough	13S/02E-32. 14S/02E-4,10,14,23,24. 14S/03E-19,30.	4376	4927
Alisal Slough	13S/02E-32. 14S/02E-4,5,9,15,16,22,23,25,26,	1520	941
Tembladero Slough	13S/02E-30,31.	1331	1784
Old Salinas River	13S/01E-36. 13S/02E-30,31. 14S/02E-6.	2553	3422
Blanco Drain	14S/02E-8,16,17,21,22,26,27,35,36. 15S/02E-1. 15S/03E-6,7.	267	335

a. Township/Range-Sections comprising each hydrologic area.
b. Endosulfan use in each year is reported in kg active ingredient summarized from the CDFA pesticide use report database.

Runoff from surrounding hills planted predominantly with strawberries is an additional source of fresh water (Fig. 3 and 4). The Moro Cojo drains directly into the lower portion of Elkhorn Slough. Runoff into Moro Cojo is predominantly from acreage planted with artichokes and strawberries. The area around Reclamation Slough, which empties into Tembladero Slough, is planted with artichokes northwest of Salinas and lettuce and cole crops southeast of Salinas. Alisal Slough also empties into Tembladero and most of the acreage draining into it is planted with lettuce, cauliflower and broccoli. Tembladero Slough drains into the Old Salinas River which then empties into the lower part of Elkhorn Slough. Tidal action then facilitates distribution of this water up and down Elkhorn Slough. Water in Blanco Drain, mostly runoff from cauliflower, cabbage and lettuce fields, is pumped into the Salinas River. The Salinas River empties into the Old Salinas River except during high water flow when it is directed into Monterey Bay, bypassing any connection with Elkhorn Slough.

Soil/Sediment Survey

In the Moss Landing drainage area, 47, 58, 58 and 39% of soil samples were positive for endosulfan I, II, sulfate and chlorthal-dimethyl residues, respectively. Maximum concentrations were 310, 960, 1300 and 690 ug/kg (dry weight) for endosulfan I, II, sulfate and chlorthal-dimethyl, respectively (Table 3).

Stewart and Cairns (1974) estimated the half-lives of endosulfan I, II and sulfate to be 60 days, 800 days and several years, respectively. Half-life estimates for chlorthal-dimethyl range from 47 days to 1 year (Walker 1978; Miller et al., 1978). In addition to heavy use of endosulfan in Moss Landing, its persistence (especially that of endosulfan II and sulfate) contributes to its predominance in soil of this region.

Of soil samples found positive for endosulfan residues (31 samples total), 58, 71 and 71% contained endosulfan I, II and sulfate, respectively. Even though the ratio of endosulfan I to II in the formulated product ranges from 3:1 to 7:3 (Ali et al., 1984; Goebel et al., 1982) endosulfan I occurs less frequently and at lower concentrations than II or sulfate presumably because of its shorter half-life. In addition, endosulfan I and II degrade in soil

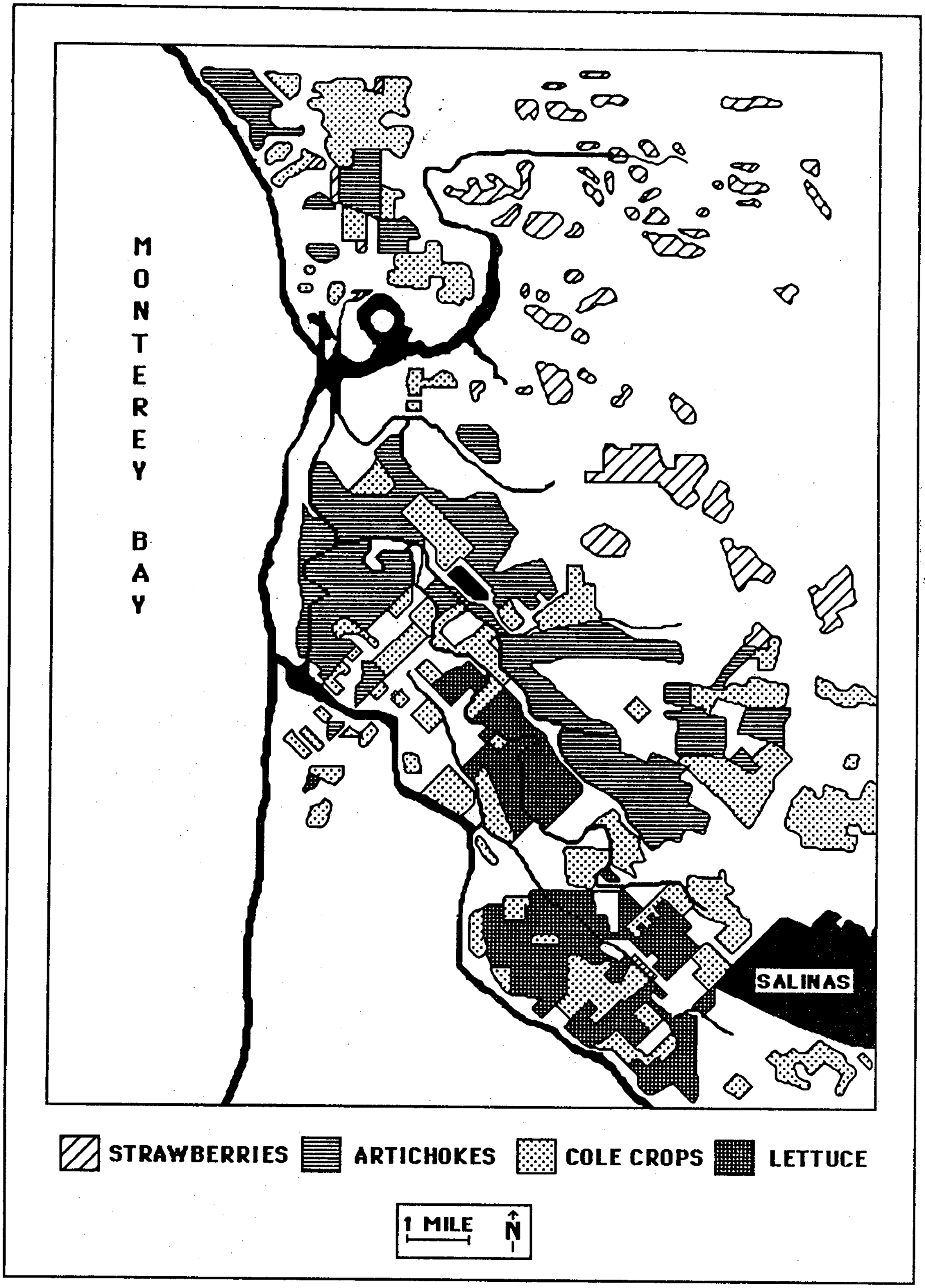

FIG. 3. LAND USE PATTERNS IN THE MOSS LANDING DRAINAGE AREA OF MONTEREY COUNTY, CALIFORNIA, 1986.

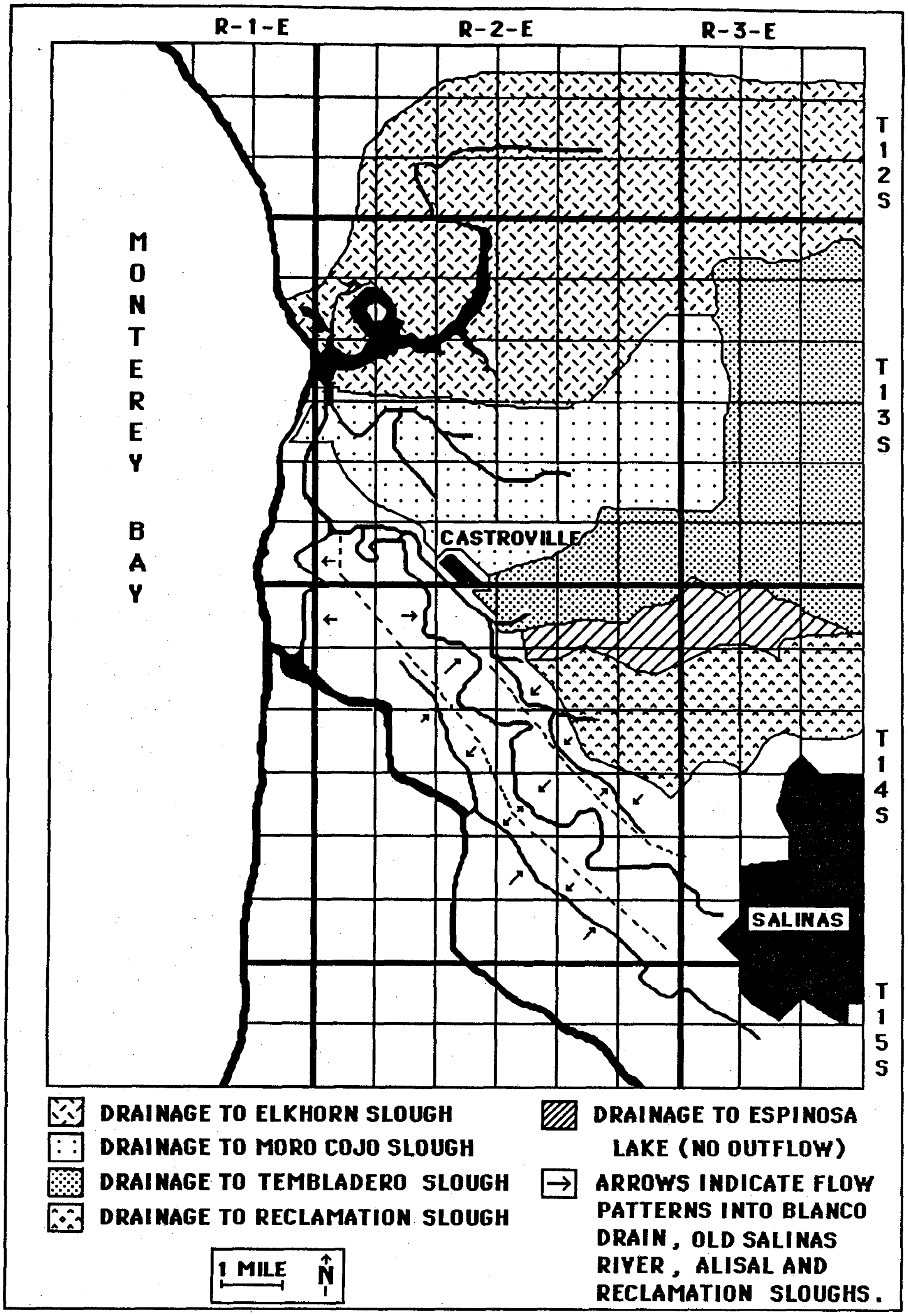

Fig. 4. HYDROLOGIC AREAS AND SURFACE WATER FLOW PATTERNS IN THE MOSS LANDING DRAINAGE AREA OF MONTEREY COUNTY, CALIFORNIA, 1986.

Table 3. Concentration of endosulfan and chlorthal-dimethyl (ug/kg, dry wt) in soil and sediment of the Moss Landing Drainage area.

		Soil				Sediment			
		Endosulfan			Chlorthal-dimethyl	Endosulfan			Chlorthal-dimethyl
Site	Location	I	II	sulfate		I	II	sulfate	
1	Elkhorn	ND[a]	8.9	18	ND	ND	ND	ND	ND
	Slough	ND	ND	ND	ND	ND	ND	ND	ND
2	Elkhorn	ND	11	ND	12	ND	ND	ND	ND
	Slough	ND	ND	ND	ND	19	ND	ND	18
3	Elkhorn	ND	4.9	11	ND	ND	ND	ND	ND
	Slough	ND	ND	9.2	ND	ND	ND	ND	ND
4	Elkhorn	ND	ND	11	49	ND	ND	27	ND
	Slough	ND	ND	ND	150	ND	ND	53	ND
5	Old Salinas	11	ND	ND	ND	ND	87	69	ND
	River	21	890	1300	ND	ND	110	76	ND
6	Old Salinas	160	800	1100	ND	ND	15	18	ND
	River	280	960	1000	11	ND	8.0	12	ND
7	Moro Cojo	260	ND	ND	ND	ND	ND	13	ND
		100	440	680	ND	ND	17	24	ND
8	Tembladero	19	250	410	ND	10	37	41	ND
	Slough	ND	770	200	ND	15	46	50	ND
9	Reclamation	6.8	ND	ND	ND	ND	12	13	ND
	Slough	ND	400	620	ND	ND	19	17	ND
10	Reclamation	ND	ND	ND	ND	30	87	100	ND
	Slough	ND	ND	ND	ND	52	160	160	ND
11	Reclamation	64	ND	ND	ND	ND	7	5	ND
	Slough	83	ND	ND	ND	ND	ND	ND	ND
12	Reclamation	310	840	1200	ND	13	23	17	ND
	Slough	160	13	ND	ND	21	57	35	ND
13	Blanco	ND	ND	ND	690	12	27	14	13
	Drain	ND	ND	ND	300	ND	ND	ND	ND
14	Blanco	ND	25	28	41	ND	25	19	25
	Drain	ND	ND	32	31	ND	17	14	12
15	Blanco	ND	58	46	48	ND	ND	ND	ND
	Drain	ND	72	58	75	ND	ND	ND	15
16	Alisal	53	ND	ND	ND	ND	21	17	ND
	Slough	34	440	1300	ND	ND	ND	ND	ND
17	Blanco	13	74	ND	43	ND	11	ND	ND
	Drain	14	74	42	34	ND	ND	ND	ND
18	Blanco	5.2	12	15	12	ND	ND	ND	ND
	Drain	ND	8.5	14	9.6	ND	ND	ND	ND
19	Alisal	ND	26	54	31	ND	ND	ND	ND
	Slough	4.2	62	48	36	ND	ND	ND	ND
20	Salinas	--[b]	--	--	--	ND	ND	ND	ND
	River	--	--	--	--	ND	ND	ND	ND

a. ND = not detected. The detection limits for endosulfan I, II, sulfate and chlorthal-dimethyl were 8.8 ug/kg in sediment, 4.4 ug/kg in soil, and 8.8 ug/kg for sulfate in soil.
b. Soil samples were not taken.

Table III-1. Endosulfan and chlorthal-dimethyl method validation study: Sediment. Analyte: endosulfan I, endosulfan II, endosulfan sulfate, chlorthal-dimethyl. Matrix: sediment, Detection Limit: 8.8 ug/kg, Laboratory: CDFA, Chemist: Karen Hefner.

CDFA Sample #	Lab Sample #	Results (ug/kg)	Spike Level (ug/kg)	Recovery %	Mean Recovery	SD	CV (%)
endosulfan I:							
3	112	13.4	20	67			
3	113	15.4	20	77			
3	114	15.4	20	77			
3	115	13.8	20	69			
3	123	16.8	20	84			
51	182	10	10	100			
51	183	10.6	10	106			
51	229	9	10	90			
51	230	8.2	10	82			
51	231	9	10	90			
51	232	9.2	10	92			
51	233	10.4	10	104			
51	283	9.8	10	98			
51	336	10.2	10	102			
51	348	20	20	100	89	12.3	13
endosulfan II:							
3	112	19.4	20	97			
3	113	19.8	20	99			
3	114	16.8	20	84			
3	115	18.8	20	94			
3	123	18.4	20	92			
51	182	10.2	10	102			
51	183	10.8	10	108			
51	229	9.6	10	96			
51	230	8.2	10	82			
51	231	8.6	10	86			
51	232	9.4	10	94			
51	233	10.4	10	104			
51	283	10	10	100			
51	336	10.2	10	102			
51	348	26	20	130	98	11.2	11
endosulfan sulfate:							
3	112	23.6	20	118			
3	113	20.6	20	103			
3	114	18.4	20	92			
3	115	25	20	125			
3	123	20.4	20	102			
51	182	9	10	90			
51	183	9.4	10	93			
51	229	10.2	10	102			
51	230	8	10	80			
51	231	8.2	10	82			
51	232	9.4	10	94			
51	233	10.4	10	104			
51	283	8.8	10	88			
51	336	9.6	10	96			
51	348	22	20	110	99	12.1	12
chlorthal-dimethyl:							
3	106	34	30	113			
3	108	32	30	107			
3	109	37.4	30	125			
3	110	28.8	30	96			
3	111	26.4	30	88			
3	120	20	20	100			
51	227	10.6	10	106			
51	226	8.4	10	84			
51	225	9	10	90			
51	224	8.8	10	88			
51	223	9.4	10	94			
51	335	11.2	10	102			
51	282	11.2	10	102			
51	181	11.8	10	107			
51	180	11.6	10	105			
51	347	20.2	22	92	100	10.4	10

Table III-2. Endosulfan and chlorthal-dimethyl method validation study. Analyte: endosulfan I, endosulfan II, endosulfan sulfate, chlorthal-dimethyl, Matrix: **Reagent spikes**, Laboratory: CDFA, Chemist: Karen Hefner.

CDFA Sample #	Lab Sample #	Results (ug)	Spike Level (ug)	Recovery %	Mean Recovery	SD
endosulfan I:						
1	199	0.46	0.5	92		
2	122	0.48	0.5	96		
3	334	0.44	0.5	88		
4	350	0.52	0.5	104	95	5.9
endosulfan II:						
1	199	0.59	0.5	118		
2	122	0.47	0.5	94		
3	334	0.42	0.5	84		
4	350	0.55	0.5	110	102	13
endosulfan sulfate:						
1	199	0.57	0.5	114		
2	122	0.5	0.5	100		
3	334	0.46	0.5	92		
4	350	0.54	0.5	108	104	8.3
chlorthal-dimethyl:						
1	198	0.5	0.5	91		
2	121	0.5	0.5	100		
3	333	0.47	0.5	94		
4	349	0.44	0.5	88	93	4.4

Table III-3. Endosulfan and chlorthal-dimethyl method validation study.
Analyte: **endolfsulfan I**
Matrix: soil, Detection Limit: 4.4 ug/kg, Laboratory: APPL,
Chemist: Jeffery C.

CDFA Sample #	Lab Sample #	Results (ug/kg)	Spike Level (ug/kg)	Recovery %	Mean Recovery	SD	CV (%)
endosulfan I:							
1		4.77	16	29.8			
2		8.75	16	54.7			
3		10.75	16	67.2			
4		5.14	16	32.1			
5		5.70	16	35.6			
6		7.81	16	48.8			
7		12.83	16	80.2			
8		6.38	16	39.9			
9		7.44	16	46.5			
10		7.95	16	49.7			
11		15.4	50	30.8			
12		12.55	50	25.1			
13		17.6	50	35.2			
14		17.45	50	34.9			
15		27.2	50	54.4			
16		15.0	50	30.0			
17		26.5	50	53.0			
18		16.3	50	32.6			
19		22.55	50	45.1			
20		17.7	50	35.4			
21		574	2000	28.7			
22		504	2000	25.2			
23		346	2000	17.3			
24		742	2000	37.1			
25		744	2000	37.2			
26		926	2000	46.3			
27		862	2000	43.1			
28		640	2000	32.0			
29		792	2000	39.6			
30		486	2000	24.3	39.7	13.1	33

Table III-4. Endosulfan and chlorthal-dimethyl method validation study.
Analyte: **endosulfan II**
Matrix: soil, Detection Limit: 4.4 ug/kg, Laboratory: APPL,
Chemist: Jeffery C.

CDFA Sample #	Lab Sample #	Results (ug/kg)	Spike Level (ug/kg)	Recovery %	Mean Recovery	SD	CV (%)
endosulfan II:							
1		26.1	32	81.6			
2		38.37	32	119.9			
3		48.0	32	150.0			
4		28.89	32	90.3			
5		30.78	32	96.2			
6		23.42	32	73.2			
7		29.18	32	91.2			
8		20.38	32	63.7			
9		12.09	32	37.8			
10		11.77	32	36.8			
11		27.79	70	39.7			
12		29.05	70	41.5			
13		39.13	70	55.9			
14		43.89	70	62.7			
15		43.47	70	62.1			
16		53.27	70	76.1			
17		45.64	70	65.2			
18		28.77	70	41.1			
19		46.41	70	66.3			
20		29.40	70	42.0			
21		2360.4	2800	84.3			
22		2083.2	2800	74.4			
23		1699.6	2800	60.7			
24		2335.2	2800	83.4			
25		2035.6	2800	72.7			
26		2612.4	2800	93.3			
27		2632.0	2800	94.0			
28		2105.6	2800	75.2			
29		2581.6	2800	92.2			
30		2072.0	2800	74.0	73.3	24.7	34

Table III-5. Endosulfan and chlorthal-dimethyl method validation study.
Analyte: **endosulfan sulfate**
Matrix: soil, Detection Limit: 8.8 ug/kg, Laboratory: APPL,
Chemist: Jeffery C.

CDFA Sample #	Lab Sample #	Results (ug/kg)	Spike Level (ug/kg)	Recovery %	Mean Recovery	SD	CV (%)
endosulfan sulfate:							
1		57.92	80	72.4			
2		73.84	80	92.3			
3		91.12	80	113.9			
4		62.56	80	78.2			
5		64.4	80	80.5			
6		42.48	80	53.1			
7		52.16	80	65.2			
8		41.92	80	52.4			
9		72.56	80	90.7			
10		68.08	80	85.1			
11		127.75	250	51.1			
12		114.25	250	45.7			
13		625.0	250	250.0			
14		106.5	250	42.6			
15		116.0	250	46.4			
16		223.25	250	89.3			
17		184.50	250	73.8			
18		133.75	250	53.5			
19		183.75	250	73.5			
20		156.0	250	62.4			
21		6710	10000	67.1			
22		6610	10000	66.1			
23		5610	10000	56.1			
24		6550	10000	65.5			
25		6010	10000	60.0			
26		7530	10000	75.3			
27		7780	10000	77.8			
28		6870	10000	68.7			
29		7210	10000	72.1			
30		6130	10000	61.3	74.7	36.1	48

Table III-6. Endosulfan and chlorthal-dimethyl method validation study.
Analyte: chlorthal-dimethyl
Matrix: soil, Detection Limit: 4.4 ug/kg, Laboratory: APPL,
Chemist: Jeffery C.

CDFA Sample #	Lab Sample #	Results (ug/kg)	Spike Level (ug/kg)	Recovery %	Mean Recovery	SD	CV (%)
chlorthal-dimethyl:							
1		5.06	18	28.1			
2		11.56	18	64.2			
3		15.70	18	87.2			
4		6.46	18	35.9			
5		16.88	18	93.8			
6		12.92	18	71.8			
7		4.68	18	26.0			
8		10.94	18	60.8			
9		7.99	18	44.4			
10		5.80	18	32.2			
11		42.0	150	28.0			
12		46.5	150	31.0			
13		58.5	150	39.0			
14		62.25	150	41.5			
15		57.45	150	38.3			
16		39.75	150	26.5			
17		85.35	150	56.9			
18		37.35	150	24.9			
19		54.0	150	36.0			
20		37.2	150	24.8			
21		3030	6000	50.5			
22		2064	6000	34.3			
23		1422	6000	23.7			
24		3354	6000	55.9			
25		3192	6000	53.2			
26		4536	6000	75.6			
27		3888	6000	64.8			
28		2568	6000	42.8			
29		3378	6000	56.3			
30		2118	6000	35.3	46.1	18.8	41

Analyte: endosulfan I, endosulfan II, endosulfan sulfate, chlorthal-dimethyl
Matrix: Sediment Date: 2/19/88
Reporting Limit (APPL): 4.4 ug/kg, 8.8 ug/kg Chemist (APPL): J.C.
Reporting Limit (CDFA): 4.4 ug/kg Chemist (CDFA): K.H.

CDFA Sample #	Lab Sample #	APPL (ug/kg)	CDFA (ug/kg)	$\bar{X}$	SD	CV (%)
endosulfan I:						
214	12792	<4.4 ug/kg				
194	191		<4.4 ug/kg			
208	12788	14				
93	275		13	13.5	0.5	4
209	12789	<4.4 ug/kg				
5	124		<4.4 ug/kg			
210	12790	<4.4 ug/kg				
115	292		<4.4 ug/kg			
213	12791	<4.4 ug/kg				
8	185		15			
endosulfan II:						
214	12792	<4.4 ug/kg				
194	191		<4.4 ug/kg			
208	12788	22.1				
93	275		23	22.5	0.4	2
209	12789	<4.4 ug/kg				
5	124		<4.4 ug/kg			
210	12790	<4.4 ug/kg				
115	292		Trace			
213	12791	<8.8 ug/kg				
8	185		46			
endosulfan sulfate:						
214	12792	<8./8 ug/kg				
194	191		Trace			
208	12788	13.6				
93	275		17	15.3	1.7	11
209	12789	<8.8 ug/kg				
5	124		13			
210	12790	<8.8 ug/kg				
115	292		Trace			
213	12791	<4.4 ug/kg				
8	185		50			
chlorthal-dimethyl:						
214	12792	<4.4 ug/kg				
194	191		<4.4 ug/kg			
208	12788	<4.4 ug/kg				
93	275		Trace			
209	12789	<4.4 ug/kg				
5	124		<4.4 ug/kg			
210	12790	<4.4 ug/kg				
115	292		Trace			
213	12791	<4.4 ug/kg				
8	185		Trace			